

The University of Chicago

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 $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-Ca}_2\text{Al}_2\text{SiO}_7\text{-NaAlSiO}_4$

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF GEOLOGY
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these compositions were in the plane of anorthite-gehlenite-nepheline + 10 per cent wollastonite, being used to locate the position of the boundary between the fields of anorthite, melilite, and nepheline as it passes through this plane of 10 per cent CaSiO_3 in the subsidiary tetrahedron. In addition, five mixtures

measured with a platinum-platinum 90 rhodium 10 thermoelement, calibrated at the melting-points of lithium metasilicate ($1,201^\circ\text{C.}$) and diopside ($1,391.5^\circ\text{C.}$). The results of quenching runs were examined microscopically to determine the nature of the phases present at equilibrium. The significant data

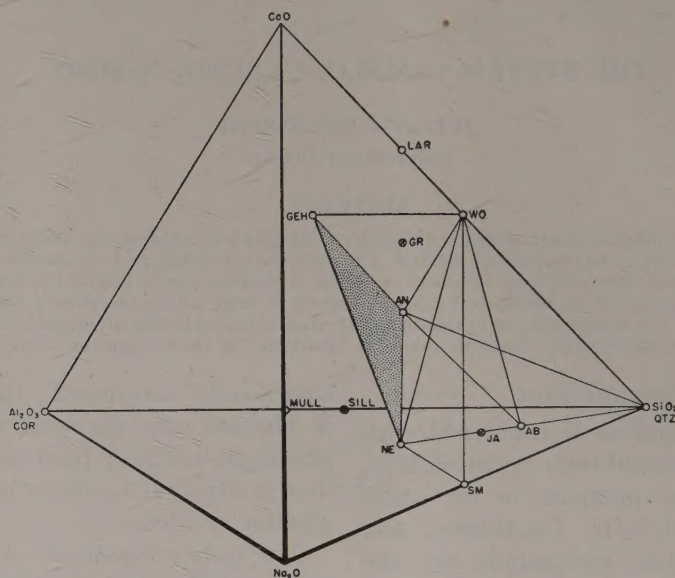


FIG. 1.—The soda-lime-alumina-silica tetrahedron. The shaded area indicates the position of the system anorthite-gehlenite-nepheline within the tetrahedron. Other internal systems that have been investigated are shown by full lines joining the composition points. The plane nepheline-gehlenite-wollastonite plus 10 per cent anorthite has also been investigated (unpublished data of H. S. Yoder). The compounds that have been prepared synthetically are shown as $\bigcirc$; those that occur in nature but that have not been synthesized are shown thus: $\otimes$.

The abbreviations signify: *AN*, anorthite; *GEH*, gehlenite; *NE*, nepheline; *WO*, wollastonite; *AB*, albite; *JA*, jadeite; *SM*, sodium metasilicate; *SILL*, sillimanite; *MULL*, mullite; *LAR*, larnite; *GR*, grossularite; *QTZ*, quartz; *COR*, corundum.

prepared and examined by H. S. Yoder¹ that fall in the plane AN-GEH-NE are incorporated with the results here presented.

The mixtures were studied as to thermal behavior by means of the quenching method developed in the Geophysical Laboratory of the Carnegie Institution of Washington.² Temperatures were

presented in Tables 1 and 2, and from these data the equilibrium diagram has been prepared.

PROPERTIES OF THE CRYSTALLINE PHASES

$\text{CaAl}_2\text{Si}_2\text{O}_8$

Pure $\text{CaAl}_2\text{Si}_2\text{O}_8$ has but one modification—anorthite—which melts at

¹ Unpublished data on the system nepheline-gehlenite-wollastonite plus 10 per cent anorthite.

² E. S. Shepherd, G. A. Rankin, and F. E. Wright, "The Binary Systems of Alumina with Silica, Lime, and Magnesia," *Amer. Jour. Sci.*, Vol. XXVIII (4th ser., 1909), p. 308.

1,552° C. It is triclinic, with $\alpha = 1.5755$, $\beta = 1.5832$, and $\gamma = 1.5885$. Crystals obtained in quenching runs are commonly platy, with 010 showing the strongest development. Albite twinning is common. The crystals encountered in this investigation are plagioclase, of a composition not far from pure anorthite, as shown by maximum index values approaching 1.588.

$\text{Ca}_2\text{Al}_2\text{SiO}_7$

Artificial gehlenite also melts congruently, at a temperature of 1,590° C.³ It is tetragonal, as tabular or short prismatic crystals. Its indices of refraction are $\omega = 1.669$ and $\epsilon = 1.658$. The melilites encountered in this study were generally tabular, thus showing positive elongation on a negative crystal. Globular to shapeless forms were also encountered, particularly in compositions close to a boundary curve. The indices of melilites forming in this system were significantly lower than those of pure gehlenite. Although the indices were accurately determined in but several runs, values as low as $\omega = 1.651$ and $\epsilon' = 1.641$ were encountered. This will be discussed in more detail in a later section concerned with substances in solid solution.

NaAlSiO_4

Carnegieite, the high-temperature modification of NaAlSiO_4 , exists in three forms, all of which are known only from synthetic melts. The highest-temperature form, which is isometric, melts at 1,526° C.⁴ and inverts to a triclinic form

³ E. F. Osborn and J. F. Schairer, "The Ternary System, Pseudo-wollastonite-Akermanite-Gehlenite," *Amer. Jour. Sci.*, Vol. CCXXXIX (1941), p. 719.

⁴ N. L. Bowen, "The Binary System: $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ (Nephelinite, Carnegieite)- $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Anorthite)," *Amer. Jour. Sci.*, Vol. XXXIII (4th ser., 1912), pp. 554 ff.

at 690° C.⁵ A second inversion, accompanied by a marked change in birefringence, occurs at 226.5° C. The indices of refraction of the low-temperature form are given by Bowen⁶ as $\alpha = 1.514$, $\beta = 1.514$, $\gamma = 1.509$. Carnegieite usually occurs in globular masses, showing no external crystal form and, typically, has intricate polysynthetic twinning that forms as a result of inversion.

Pure artificial nepheline inverts to carnegieite at a temperature of $1,254 \pm 5^\circ$ C.⁷ Bowen⁸ found that anorthite, which may go into solid solution with nephelinite to the extent of 35 per cent, raises the inversion temperature 100° C., while albite in solid solution brings about a rise of 30° at its maximum concentration.⁹ Smalley, in investigating the system NaAlSiO_4 - $\text{Ca}_2\text{Al}_2\text{SiO}_7$, found an inversion range extending from about 50° above, to 100° below, the normal inversion point.¹⁰ However, the nonbinary nature of the system precluded making any assured statement as to the exact nature of the solid solution.

Nepheline is hexagonal and crystallizes from melts as prismatic crystals with basal pinacoid. The indices as determined by Bowen on the pure synthetic material are $\epsilon = 1.533$ and $\omega = 1.537$.¹¹ He found that the indices of the limiting anorthite-nepheline solid solution are

⁵ N. L. Bowen and J. W. Greig, "The Crystalline Modifications of NaAlSiO_4 ," *Amer. Jour. Sci.*, Vol. X (5th ser., 1925), pp. 208-10.

⁶ P. 564 of ft. n. 4.

⁷ J. W. Greig and Tom. F. W. Barth, "The System $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (Nephelinite, Carnegieite)- $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (Albite)," *Amer. Jour. Sci.*, Vol. XXXV+A (5th ser., 1938) p. 108.

⁸ P. 571 of ft. n. 4.

⁹ P. 109 of ft. n. 7.

¹⁰ Robert G. Smalley, "The System NaAlSiO_4 - $\text{Ca}_2\text{Al}_2\text{SiO}_7$," *Jour. Geol.*, Vol. LV, No. 1 (January, 1947), p. 28.

¹¹ P. 566 of ft. n. 4.

$\epsilon = 1.539$, $\omega = 1.537$, while solid solution of albite in nepheline has been found to lower the indices of the latter somewhat.¹² Unusually high indices were noted by Smalley in nephelines crystallizing from the system $\text{NaAlSiO}_4\text{--Ca}_2\text{Al}_2\text{SiO}_7$, values as high as 1.552 being reached in crystals from melts having 35 per cent gehlenite.¹³ The present study indicates that the solid solution responsible for this rise remains effective upon addition of $\text{CaAl}_2\text{Si}_2\text{O}_8$, as values of $\omega = 1.548$ and $\epsilon > 1.548$ were obtained from runs at a composition of approximately 35 per cent nepheline, 20 per cent gehlenite, and 45 per cent anorthite.

$\beta\text{-Al}_2\text{O}_3$

The $\beta\text{-Al}_2\text{O}_3$ here encountered occurs in thin hexagonal plates, exhibiting high relief and high birefringence when viewed on edge. Parallel extinction and positive elongation are shown, the sign of elongation coupled with the platy habit indicating that the crystals are optically negative. No indices were determined, but G. A. Rankin and H. E. Merwin gave the values $\omega = 1.677 \pm .003$ and $\epsilon = 1.635\text{--}1.650$ for the $\beta\text{-Al}_2\text{O}_3$ found in preparations thought to be pure alumina.¹⁴ Rankin and Merwin determined the melting-point as $2,050^\circ \pm 20^\circ \text{C}$.

The exact relations of $\beta\text{-Al}_2\text{O}_3$ to the other known forms of Al_2O_3 are not completely understood. The indices are considerably lower than those of corundum, and chemical and X-ray analyses indicate that soda is present in the structure. On the basis of X-ray work the formula

$\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ was proposed by C. A. Beevers and M. A. S. Ross,¹⁵ whereas W. L. Bragg, C. Gottfried, and J. West had somewhat earlier determined it as $\frac{1}{2} \text{Na}_2\text{O} \cdot 11\frac{1}{2} \text{Al}_2\text{O}_3$.¹⁶

Recent work at the Geophysical Laboratory of the Carnegie Institution of Washington has shown that $\beta\text{-Al}_2\text{O}_3$ is converted to corundum when held at elevated temperatures for long periods,¹⁷ indicating that $\beta\text{-Al}_2\text{O}_3$ is metastable. The melting-point as determined by Rankin and Merwin is almost exactly that of pure $\alpha\text{-Al}_2\text{O}_3$, so it is likely that their crystals had undergone the conversion to corundum before melting. It is possible that $\beta\text{-Al}_2\text{O}_3$ is an example of a "stuffed lattice," in which Na atoms assume random interstitial positions in the network. Certain soda-bearing tridymites have been interpreted in this way by M. J. Buerger.¹⁸ This explanation would account for the disagreements of different investigators, as it does not require any fixed ratio of soda to alumina. It is also consistent with the findings of the Geophysical Laboratory, as the Na atoms, given sufficient time, might tend to be "squeezed out" of the structure.

PREVIOUS INVESTIGATIONS

THE SYSTEM $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$

The system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$ was investigated by Bowen,¹⁹ and his equilibrium diagram is shown in Figure 2, with modifications based on work of

¹⁵ "The Crystal Structure of $\beta\text{-Al}_2\text{O}_3$," *Zeitschr. f. Kryst. u. Min.*, Vol. XCVII (1937), pp. 59-66.

¹⁶ "The Structure of $\beta\text{-Al}_2\text{O}_3$," *Zeitschr. f. Kryst. u. Min.*, Vol. LXXVII (1931), pp. 255-74.

¹⁷ J. F. Schairer and N. L. Bowen, "Melting Relations in the Systems $\text{Na}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$ and $\text{K}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$," *Amer. Jour. Sci.*, Vol. CCXLV (April, 1947) pp. 193-204.

¹⁸ *Science*, Vol. XCV (1942), pp. 20-21.

¹⁹ Pp. 551-73 of ftn. 4.

¹² W. R. Foster, "The System $\text{NaAlSi}_3\text{O}_8\text{--CaSiO}_3\text{--NaAlSiO}_4$," *Jour. Geol.*, Vol. L (1942), p. 157.

¹³ P. 28 of ftn. 10.

¹⁴ "The Ternary System $\text{CaO--Al}_2\text{O}_3\text{--MgO}$," *Jour. Amer. Chem. Soc.*, Vol. XXXVIII (1916), pp. 566-88.

J. F. Schairer²⁰ and of W. K. Gummer.²¹ This system exhibits partial solid solution between the two end-members, complicated by the carnegieite-nepheline inversion. It was, in fact, the first-found example in silicates of the combined phenomena of solid solution and enantiotropism theoretically proposed by Roozeboom. The eutectic was placed at 46 per cent anorthite by Bowen and at a temperature of $1,304^\circ\text{C}$. The inversion takes place at $1,352^\circ\text{C}$., a rise of 104°

tem NaAlSiO_4 - $\text{CaAl}_2\text{Si}_2\text{O}_8$ - SiO_2 , Schairer²² found β - Al_2O_3 in mixtures adjacent to the nepheline-anorthite join; and, on preparing mixtures along that join, he also found a considerable range in which β - Al_2O_3 is the primary phase. This work was somewhat amplified by Gummer,²³ who determined the extent of the field of β - Al_2O_3 in the system CaSiO_3 - $\text{CaAl}_2\text{Si}_2\text{O}_8$ - NaAlSiO_4 . The liquidus for β - Al_2O_3 has not been definitely established as yet, but its outline, based on

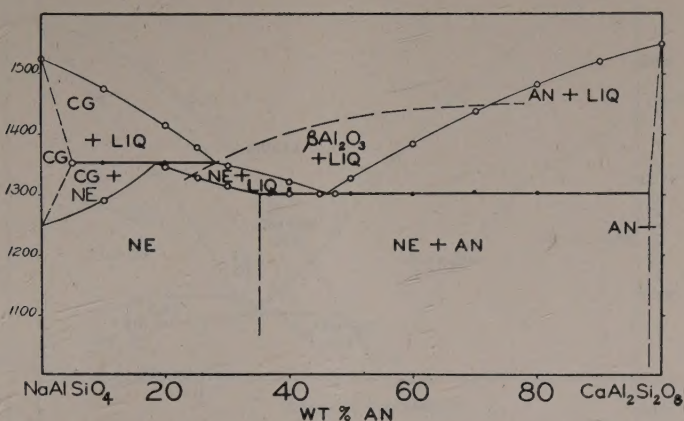


FIG. 2.—Equilibrium diagram for the system $\text{CaAl}_2\text{Si}_2\text{O}_8$ - NaAlSiO_4 (after Bowen, with modifications after work by Schairer and Gummer).

above the inversion in pure NaAlSiO_4 , as a result of the solid solution of anorthite in nepheline to the extent of 35 weight per cent. Carnegieite takes but approximately 5 per cent anorthite in solid solution.

Bowen encountered "alumina" in some of his mixtures and accounted for it by soda volatilization at the high temperatures required for fusion of the glasses. This actually occurs but is only part of the story. The β -form was at that time unknown, but, in investigating the sys-

tem the evidence on hand, is shown by a dashed line on the diagram.

This intrusion of a field of β - Al_2O_3 upsets the binary nature of the system. The field of nepheline plus liquid is actually a field of β - Al_2O_3 , nepheline, and liquid; and much of the field of anorthite plus liquid, as determined by Bowen, is also a ternary field of β - Al_2O_3 , anorthite, and liquid. The subliquidus extent of the field of β - Al_2O_3 has not been determined, but Gummer's work indicates that it is present in several mixtures at $1,200^\circ\text{C}$.

²⁰ Unpublished data.

²¹ "The System CaSiO_3 - $\text{CaAl}_2\text{Si}_2\text{O}_8$ - NaAlSiO_4 ," *Jour. Geol.*, Vol. LI, No. 8 (November-December, 1943), pp. 508-9.

²² Unpublished data.

²³ Pp. 508-9 of ftn. 21.

THE SYSTEM $\text{NaAlSiO}_4\text{--Ca}_2\text{Al}_2\text{SiO}_7$

The equilibrium diagram of this system is presented in Figure 3, as determined by Smalley.²⁴ The unusual nature of this system merits some discussion, which is here presented largely as taken from Smalley's work. In his words: "Even a casual inspection of the equilibrium diagram will suffice to show that this is not a true binary system."²⁵

The inversion relations are further complicated by the unique occurrence, near the pseudoeutectic, of nepheline in equilibrium with liquid at higher temperatures than is carnegieite.

In several fields of this system three phases occur in equilibrium, and in one field four phases are present. Consideration of the phase rule, $P + F = C + 1$, as applied to systems in which the vapor

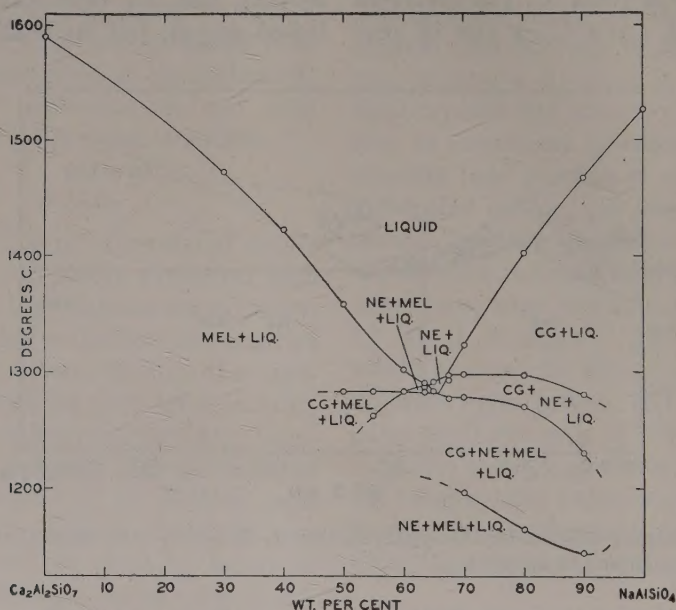


FIG. 3.—Equilibrium diagram for the system $\text{NaAlSiO}_4\text{--Ca}_2\text{Al}_2\text{SiO}_7$ (after Smalley)

Variations in optical properties of all three of the crystalline phases are indicative of solid solutions; that the solid solutions cannot be expressed in terms of the end-members is obvious from the diagram. The lack of a binary eutectic, of simple solidus curves and the persistence of the liquid phase down to the lowest temperatures of observation, as well as the previously mentioned large temperature range of inversion on both sides of the pseudoeutectic composition, all attest to the nonbinary nature of the

phase is negligible, indicates that in a binary system a maximum of three phases can coexist in equilibrium, and then only at a fixed temperature. Thus the existence of four phases within a temperature composition range requires four components—the four constituent oxides. The join $\text{NaAlSiO}_4\text{--Ca}_2\text{Al}_2\text{SiO}_7$ is therefore quaternary in nature, and the composition of the phases cannot be represented in the plane of the diagram but must be viewed in terms of the parent-tetrahedron.

The junction of the liquidus curves is

²⁴ Pp. 27–37 of ftn. 10.

²⁵ P. 31 of ftn. 10.

at 64 per cent NaAlSiO_4 at a temperature of $1,287^\circ\text{C}$. This pseudoeutectic is actually divariant, representing the trace of the boundary line between the fields of nepheline solid solution and melilite in the quaternary system. The junction of the carnegieite liquidus with the nepheline liquidus occurs at 67 per cent NaAlSiO_4 and at $1,297^\circ\text{C}$. Just as the pseudoeutectic is not invariant, so these liquidus curves are not univariant but

used in constructing the equilibrium diagram of Figure 4. The system shows none of the complications of the preceding limiting systems. The eutectic is at 51.7 per cent anorthite and at a temperature of $1,387^\circ \pm 2^\circ\text{C}$.

THE THERMAL DATA

The thermal data necessary for establishing the equilibrium relationships in the system $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ -

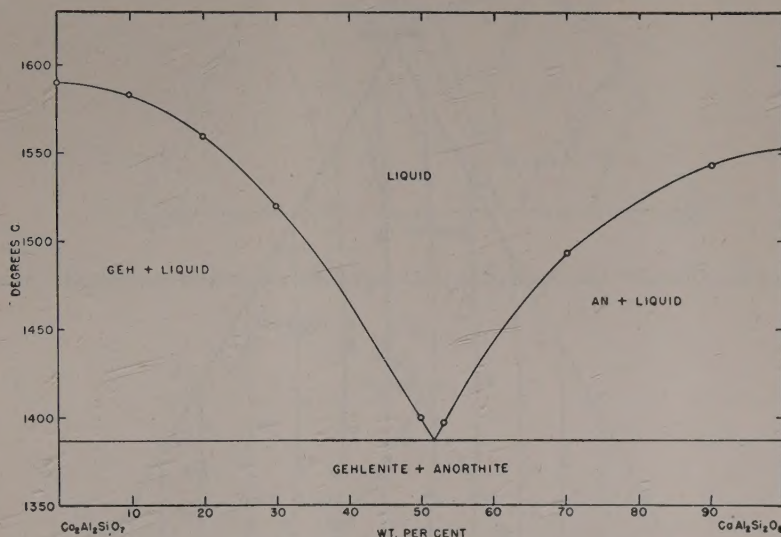


FIG. 4.—Equilibrium diagram for the binary system $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (after Rankin and Wright, as revised by E. F. Osborn).

trivariant, and the curves do not give the compositions of the liquids in equilibrium with the solid phases at the various temperatures.

THE BINARY SYSTEM $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$

The binary system $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ was first investigated by G. A. Rankin and F. E. Wright in their work on the system CaO - Al_2O_3 - SiO_2 .²⁶ The binary join has been revised by E. F. Osborn,²⁷ and his data are here

²⁶ "The Ternary System of CaO - Al_2O_3 - SiO_2 ," *Amer. Jour. Sci.*, Vol. XXXIX (4th ser., 1915), pp. 1-79.

NaAlSiO_4 are presented in Table 1, and the diagrams based on these results are shown in Figures 6 and 7. In Figure 6 are shown the isotherms at 50° intervals, while in Figure 7 the isotherms have been omitted, the stability fields have been labeled, and arrows have been inserted to indicate the directions of falling temperature. Figure 5 is a composition-refractive index²⁸ diagram of the homogeneous glasses prepared in this plane.

²⁷ Unpublished data.

²⁸ Sodium-vapor light was used for all refractive index measurements in this study.

NONTERNARY NATURE OF THE SYSTEM

The system is not a true ternary system; indeed, it is quaternary throughout, since a field of basic plagioclase is present rather than one of anorthite, a field of melilite instead of gehlenite, and carnegieite and nepheline also form solid solutions that cannot be expressed in terms of the three end-members. The field of β - Al_2O_3 encroaches upon the system as

THE LIQUIDUS RELATIONS

The five fields of the primary phases are, in order of decreasing size, melilite, plagioclase, nepheline solid solutions, carnegieite solid solutions, and β -alumina. The configuration of the fusion surfaces can be ascertained from the isotherms of Figure 6. The carnegieite surface dips rather sharply into the adjoining fusion surface of nepheline, which

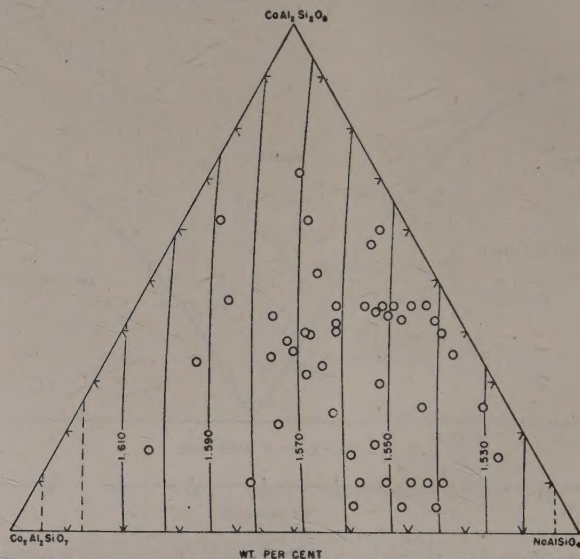


FIG. 5.—Composition-refractive-index diagram for the glass mixtures

an extension of the quaternary field of alumina originating at the Al_2O_3 corner of the tetrahedron. The system is thus quite complex, the composition of any liquid upon crystallization does not remain in the plane defined by the three end-members; courses of crystallization can be discussed only in terms of the parent-soda-lime-alumina-silica system. A more complete discussion as to the nonternary behavior of mixtures in this plane will be presented in a following section on courses of crystallization.

is relatively flat. The surfaces of melilite and plagioclase are convex and slope toward the center of the system. The fusion surface of β - Al_2O_3 is but tentatively indicated, owing to the somewhat uncertain data on the liquidus relations along the NaAlSiO_4 - $\text{CaAl}_2\text{Si}_2\text{O}_8$ join.

A maximum is present on the boundary curve between the fields of melilite and nepheline solid solutions. This maximum, the position of which is indicated by the curvature of the $1,300^\circ\text{C}$. iso-

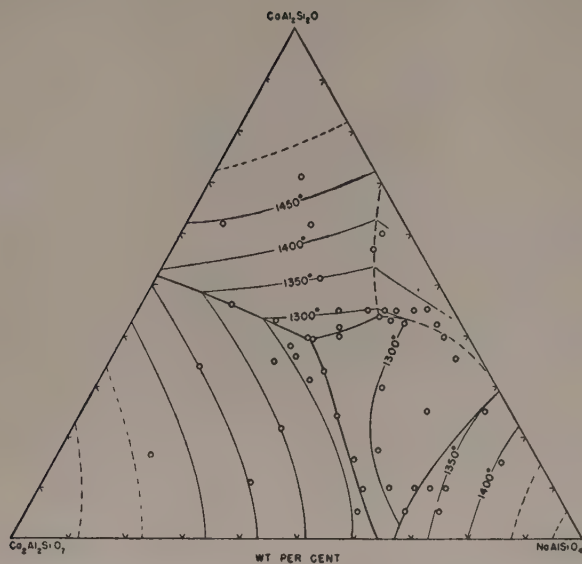


FIG. 6.—Equilibrium diagram for the system $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ - NaAlSiO_4 , with isotherms

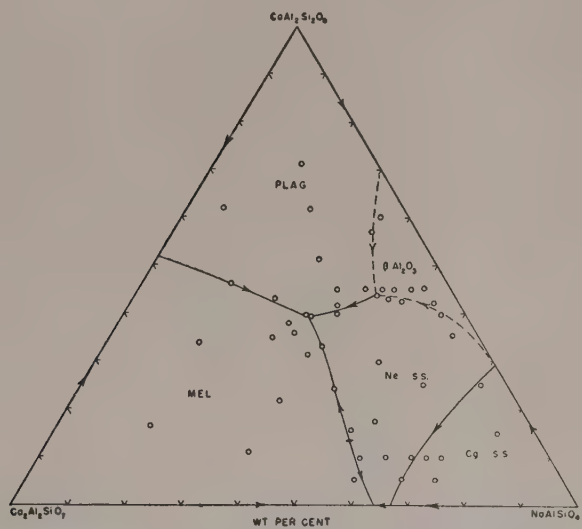


FIG. 7.—Equilibrium diagram for the system $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ - NaAlSiO_4 , with isotherms omitted

TABLE 1
THERMAL DATA FOR THE SYSTEM $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ - NaAlSiO_3

WEIGHT PER CENT			TIME (MINUTES)	TEMPERATURE (° C.)	FINAL CONDITION
CaAl ₂ Si ₂ O ₈	Ca ₂ Al ₂ SiO ₇	NaAlSiO ₄			
Primary-Phase Melilite					
31.3	32	36.7	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1299 \\ 1295 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, rare MEL} \end{matrix}$
5.2	36.8	58	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1296 \\ 1292 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, MEL} \end{matrix}$
33.1	28.5	38.4	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1278 \\ 1274 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, NE, rare MEL} \end{matrix}$
24	31	45	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1288 \\ 1284 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, NE, rare MEL} \end{matrix}$
46	38.1	15.9	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1328 \\ 1324 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, MEL, rare AN} \end{matrix}$
21.7	41.8	36.5	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1352 \\ 1348 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, MEL} \end{matrix}$
11	52.6	36.4	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1399 \\ 1395 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, MEL} \end{matrix}$
34	50	16	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1407 \\ 1403 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, rare MEL} \end{matrix}$
36	32	32	$\begin{Bmatrix} 30 \\ 30 \\ 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1293 \\ 1289 \\ 1259 \\ 1242 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, MEL} \\ \text{Glass, MEL, NE} \\ \text{Glass, MEL, NE, AN} \end{matrix}$
38	32	30	$\begin{Bmatrix} 30 \\ 30 \\ 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1293 \\ 1289 \\ 1259 \\ 1255 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, MEL} \\ \text{Glass, MEL, rare AN} \\ \text{Glass, MEL, AN, NE} \end{matrix}$
35	36 $\frac{1}{3}$	28 $\frac{2}{3}$	$\begin{Bmatrix} 30 \\ 30 \\ 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1319 \\ 1315 \\ 1259 \\ 1255 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, MEL} \\ \text{Glass, MEL} \\ \text{Glass, MEL, NE, AN} \end{matrix}$
16.4	67.1	16.5	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1491 \\ 1486 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, MEL} \end{matrix}$
Primary-Phase Anorthite					
71.3	13.4	15.3	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1469 \\ 1465 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass and AN} \end{matrix}$
39.7	28.1	32.2	$\begin{Bmatrix} 30 \\ 30 \\ 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1269 \\ 1267 \\ 1264 \\ 1260 \end{matrix}$	$\begin{matrix} \text{All glass} \\ \text{Glass, rare AN} \\ \text{Glass, AN, MEL} \\ \text{Glass, AN, MEL, NE} \end{matrix}$

TABLE 1—*Continued*

WEIGHT PER CENT			TIME (MINUTES)	TEMPERA- TURE (° C.)	FINAL CONDITION
CaAl ₂ Si ₂ O ₈	Ca ₂ Al ₂ SiO ₇	NaAlSiO ₄			
Primary-Phase Anorthite—Continued					
45	20	35	$\left\{ \begin{array}{l} 30 \\ 30 \\ 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1306 \\ 1302 \\ 1259 \\ 1251 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, rare AN} \\ \text{Glass, AN, NE} \\ \text{Glass, AN, NE, MEL} \end{array}$
45	15	40	$\left\{ \begin{array}{l} 30 \\ 30 \\ 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1302 \\ 1298 \\ 1288 \\ 1280 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, rare AN} \\ \text{Glass, AN} \\ \text{Glass, AN, NE} \end{array}$
57	8	35	$\left\{ \begin{array}{l} 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1376 \\ 1372 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, rare } \beta\text{-Al}_2\text{O}_3, \text{ AN} \end{array}$
41.5	21.8	36.7	$\left\{ \begin{array}{l} 30 \\ 30 \\ 30 \\ 30 \\ 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1283 \\ 1279 \\ 1275 \\ 1271 \\ 1250 \\ 1242 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, rare AN} \\ \text{Glass, AN} \\ \text{Glass, AN, NE} \\ \text{Glass, AN, NE} \\ \text{Glass, AN, NE, MEL} \end{array}$
46	38.1	15.9	$\left\{ \begin{array}{l} 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1328 \\ 1324 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, MEL, rare AN} \end{array}$
43	32	25	$\left\{ \begin{array}{l} 30 \\ 30 \\ 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1298 \\ 1294 \\ 1289 \\ 1285 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, very rare AN} \\ \text{Glass, AN} \\ \text{Glass, AN, rare MEL} \end{array}$
51.3	20.1	28.6	$\left\{ \begin{array}{l} 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1352 \\ 1348 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, AN} \end{array}$
61.8	16.6	21.6	$\left\{ \begin{array}{l} 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1422 \\ 1416 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, AN} \end{array}$
62	31.7	6.3	$\left\{ \begin{array}{l} 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1449 \\ 1445 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, AN} \end{array}$
Primary-Phase Nepheline					
15 $\frac{2}{3}$	32	52 $\frac{2}{3}$	$\left\{ \begin{array}{l} 30 \\ 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1295 \\ 1291 \\ 1287 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, NE} \\ \text{Glass, NE, MEL} \end{array}$
33.1	28.5	38.4	$\left\{ \begin{array}{l} 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1278 \\ 1274 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, NE, rare MEL} \end{array}$
24	31	45	$\left\{ \begin{array}{l} 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1288 \\ 1284 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, NE, rare MEL} \end{array}$
42.4	9.9	47.7	$\left\{ \begin{array}{l} 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1302 \\ 1298 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, NE} \end{array}$
43	12	45	$\left\{ \begin{array}{l} 30 \\ 30 \end{array} \right.$	$\begin{array}{l} 1297 \\ 1293 \end{array}$	$\begin{array}{l} \text{All glass} \\ \text{Glass, NE} \end{array}$

TABLE 1—Continued

WEIGHT PER CENT			TIME (MINUTES)	TEMPERA- TURE (° C.)	FINAL CONDITION
CaAl ₂ Si ₂ O ₈	Ca ₂ Al ₂ SiO ₇	NaAlSiO ₄			
Primary-Phase Nepheline—Continued					
35.6	4.4	60	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1329 \\ 1325 \end{matrix}$	All glass Glass, NE
39.8	4.4	55.8	$\begin{Bmatrix} 30 \\ 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1319 \\ 1315 \\ 1298 \end{matrix}$	All glass Glass, NE Glass, NE, rare β -Al ₂ O ₃
5.2	28.4	66.4	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1306 \\ 1302 \end{matrix}$	All glass Glass, NE-CG
40	22.6	37.4	$\begin{Bmatrix} 30 \\ 30 \\ 30 \\ 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1273 \\ 1269 \\ 1265 \\ 1250 \\ 1246 \end{matrix}$	All glass Glass, NE Glass, NE, AN Glass, NE, AN Some glass, NE, AN, MEL
17.4	27	55.6	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1304 \\ 1302 \end{matrix}$	All glass Glass, rare NE
29.7	20	50.3	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1306 \\ 1302 \end{matrix}$	All glass Glass, extremely rare NE
39 $\frac{1}{2}$	27 $\frac{1}{2}$	33 $\frac{1}{2}$	$\begin{Bmatrix} 30 \\ 30 \\ 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1269 \\ 1267 \\ 1263 \\ 1259 \end{matrix}$	All glass Glass, rare NE Glass, NE, MEL Glass, NE, MEL, rare AN
25.1	14.8	60.1	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1327 \\ 1323 \end{matrix}$	All glass Glass, NE
Primary-Phase Carnegieite					
5.1	22.6	72.3	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1357 \\ 1353 \end{matrix}$	All glass Glass, CG
25.1	4.4	70.5	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1358 \\ 1354 \end{matrix}$	All glass Glass, CG
5.2	28.4	66.4	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1306 \\ 1302 \end{matrix}$	All glass Glass, NE-CG
15.1	6.6	78.3	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1406 \\ 1402 \end{matrix}$	All glass Glass, abundant CG
Primary-Phase β -Al ₂ O ₃					
45.2	4.4	50.4	$\begin{Bmatrix} 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1338 \\ 1342 \end{matrix}$	Glass, very rare β -Al ₂ O ₃ All glass
45	7	48	$\begin{Bmatrix} 30 \\ 30 \\ 30 \\ 30 \end{Bmatrix}$	$\begin{matrix} 1323 \\ 1319 \\ 1297 \\ 1280 \end{matrix}$	All glass Glass, rare β -Al ₂ O ₃ Glass, sparse β -Al ₂ O ₃ Glass, NE, AN

TABLE 1—Continued

WEIGHT PER CENT			TIME (MINUTES)	TEMPERA- TURE (° C.)	FINAL CONDITION
CaAl ₂ Si ₂ O ₈	Ca ₂ Al ₂ SiO ₇	NaAlSiO ₄			
Primary-Phase β -Al ₂ O ₃ —Continued					
45	10	45	$\begin{cases} 30 \\ 30 \end{cases}$	$\begin{matrix} 1302 \\ 1306 \end{matrix}$	Glass, rare β -Al ₂ O ₃ All glass
45	12	43	$\begin{cases} 30 \\ 30 \end{cases}$	$\begin{matrix} 1306 \\ 1302 \end{matrix}$	All glass Glass, rare β -Al ₂ O ₃
60	5	35	$\begin{cases} 30 \\ 30 \\ 30 \\ 30 \end{cases}$	$\begin{matrix} 1393 \\ 1389 \\ 1384 \\ 1376 \end{matrix}$	All glass Glass, rare β -Al ₂ O ₃ Glass, β -Al ₂ O ₃ Glass, β -Al ₂ O ₃ , AN
43.9	13.6	42.5	$\begin{cases} 30 \\ 30 \\ 30 \end{cases}$	$\begin{matrix} 1294 \\ 1292 \\ 1288 \end{matrix}$	All glass Glass, very rare β -Al ₂ O ₃ Glass, NE, AN, β -Al ₂ O ₃
57	8	35	$\begin{cases} 30 \\ 30 \end{cases}$	$\begin{matrix} 1376 \\ 1372 \end{matrix}$	All glass Glass, rare β -Al ₂ O ₃ , AN
42.2	4.4	53.4	$\begin{cases} 30 \\ 30 \end{cases}$	$\begin{matrix} 1322 \\ 1318 \end{matrix}$	All glass Glass, rare β -Al ₂ O ₃

YODER'S POINTS (UNPUBLISHED)

WEIGHT PER CENT			LIQUIDUS TEMPERATURE
CaAl ₂ Si ₂ O ₈	Ca ₂ Al ₂ SiO ₇	NaAlSiO ₄	
Primary-Phase Nepheline			
10	33.3	56.7	1288° (checked), MEL at 1286°
10	28.8	61.2	1298° redetermined at 1302°
10	24.3	65.7	1314°
Primary-Phase Carnegieite			
10	21.6	68.4	1331°
10	18.9	71.1	1348°

therms in the two fields, is not very pronounced; it is but 3° higher than the temperature of the pseudoeutectic on the limiting NaAlSiO_4 - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ join. In a truly ternary system there is a maximum temperature on the boundary curve at the point where the line joining the composition of the two solid phases in equilibrium with a liquid intersects the boundary curve. This fact can sometimes be used as an indication of the composition of the solid phases, but no such interpretation can be made in the present case. The compositions of the phases do not lie in the plane of the system, and the solid solutions cannot be treated in ternary fashion. It does not necessarily follow that a composition on the gehlenite-nepheline side of the maximum will completely crystallize as some point "below" the maximum, i.e., in a direction away from anorthite, as it would if the maximum were present in the boundary curve of a ternary system.

The junction of the fields of plagioclase, melilite, and nepheline solid solutions is at a composition approximately $39\frac{1}{2}$ per cent anorthite, $27\frac{1}{2}$ per cent gehlenite, and 33 per cent nepheline and at a temperature of $1,266^\circ\text{C}$. This point is not a ternary eutectic, as crystallization is not completed at the temperature indicated ($1,266^\circ$), nor does this point represent the composition of the last residual liquid. It is merely the intersection of the plane of the system with the univariant boundary curve between the quaternary fields of melilite, plagioclase, and nepheline solid solutions.

The boundary curves are not curves of univariant equilibrium but are divariant; the change in composition of a liquid in the system that is undergoing crystallization is not along a boundary curve, as it is in a ternary system. The nepheline solid solution-carnegieite solid solution boundary curve is not an isotherm, as

the two extremities are not at the same temperature. Inversion from the high- to the low-temperature form begins at $1,352^\circ\text{C}$. at the $\text{CaAl}_2\text{Si}_2\text{O}_8$ - NaAlSiO_4 join, and at $1,297^\circ\text{C}$. at the $\text{Ca}_2\text{Al}_2\text{SiO}_7$ - NaAlSiO_4 join, with intermediate temperatures along the boundary between the two.

THE PLANE $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ -
 NaAlSiO_4 PLUS 10 PER
CENT CaSiO_3

To obtain more definite information on courses of crystallization, and, by so doing, to obtain some information as to the composition of the mix-crystals (with particular reference to the melilites) that form from melts in this system, it was deemed desirable to trace the course of the boundary curve between the fields of plagioclase, melilite, and nepheline solid solutions within the quaternary system. As has been seen, the pseudoeutectic point marks the position and temperature of this curve as it passes through the plane of the system here studied.

The technique used was to locate the pseudoeutectic (the point where plagioclase, melilite, and nepheline solid solutions crystallize simultaneously) in some other plane of the tetrahedron. The plane of $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ - NaAlSiO_4 plus 10 per cent CaSiO_3 within the subsidiary tetrahedron anorthite-gehlenite-nepheline-wollastonite was chosen as a convenient one. Figure 8 represents the subsidiary tetrahedron, oriented as in Figure 1 but removed from the parent-tetrahedron and enlarged for clarity. The dotted lines indicate the plane of 10 per cent wollastonite. The location of the pseudoeutectic was determined in this plane with but three quenching runs, and the third composition that was made up fortunately corresponded exactly with the desired point on the

boundary curve. These data are given in Table 2.

There have now been located two points on the univariant boundary curve in the quaternary system between the fields of plagioclase, melilite, and nepheline solid solutions. The two four-phase points have the following parameters:

1. Composition = $39\frac{1}{2}$ per cent anorthite, $27\frac{1}{2}$ per cent gehlenite, 33 per cent nepheline; temperature = 1266°C .
2. Composition = 35.7 per cent anorthite, 17.8 per cent gehlenite, 36.5 per cent nepheline, 10 per cent wollastonite; temperature = 1248°C .

If this curve were to be accurately determined, numerous points within the quaternary system would have to be located. It is here assumed that a straight line joining the two determined points represents the boundary curve. If this curve is to be used as a reference line, the temperature gradient along it must also be known; and again the assumption is made that a linear relationship holds, defined by the temperatures of the two measured points. That these assumptions are not entirely correct can be shown by consideration of the system $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$.²⁹ This system, which forms one face of the subsidiary tetrahedron as shown in Figure 8, is encroached upon by the field of melilite. Therefore, at the junction of the fields of melilite, plagioclase, and nepheline solid solutions, there is located a third point on the quaternary boundary curve. Gummer's diagram³⁰ shows this point to be approximately 34 per cent anorthite, 38 per cent nepheline, and 28 per cent wollastonite, and at a temperature of $1,190^\circ\text{C}$. Consideration of the three points shows that the temperature drop along the boundary is not linear, and a projection of the compositions of

the three indicates that the boundary is not straight. The departure from linearity between the values of 0–28 per cent CaSiO_3 is not considerable, however, and errors introduced by assuming linear values between 0 and 10 per cent CaSiO_3 are small enough to justify the assumptions. The complications introduced by solid solutions bring up the possibility of a temperature maximum along the

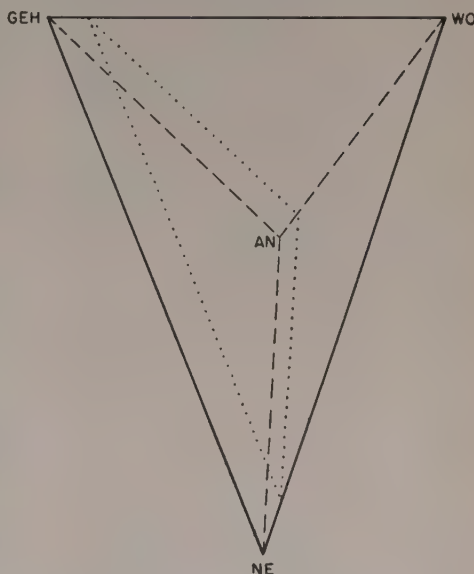


FIG. 8.—The subsidiary tetrahedron AN-GEH-NE-WO, showing (dotted lines) plane of 10 per cent WO.

boundary curve, in which case any assumptions as to temperature gradient are, of course, nullified. It is not probable that such a situation exists, however, in the limited extent of the boundary under consideration. Thus knowledge of the temperature at which nepheline solid solution and plagioclase simultaneously crystallize fixes the composition of the liquid at a point on the boundary curve corresponding to this temperature.

COURSES OF CRYSTALLIZATION

The fact that the composition of the crystalline phases does not lie in the plane

²⁹ See fn. 21.

³⁰ P. 515 of fn. 21.

of the system and, consequently, that the residual liquids resulting from crystallization also leave this plane makes difficult the tracing of courses of crystallization. If the compositions of the solid solutions were precisely known, the courses of crystallization viewed in three dimensions within the quaternary system could be precisely described. The present state of uncertainty as to the composition of

described by N. L. Bowen.³¹ In the present investigation the method used was to locate a composition in the melilite field from which plagioclase and nepheline solid solutions simultaneously crystallized as secondary phases. The significance of the simultaneous crystallization of the secondary phases is that the crystallization of the primary phase, melilite, results in a liquid of changing

TABLE 2
THERMAL DATA FOR THE PLANE $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--Ca}_2\text{Al}_2\text{SiO}_7\text{--NaAlSiO}_4 + 10$ PER CENT CaSiO_3

WEIGHT PER CENT				TIME (MINUTES)	TEMPERATURE (° C.)	FINAL CONDITION
CaAl ₂ Si ₂ O ₈	Ca ₂ Al ₂ SiO ₇	NaAlSiO ₄	CaSiO ₃			
Primary-Phase Melilite						
37 $\frac{2}{3}$	21 $\frac{2}{3}$	30 $\frac{2}{3}$	10	$\begin{cases} 30 \\ 30 \\ 30 \end{cases}$	$\begin{matrix} 1275 \\ 1271 \\ 1263 \end{matrix}$	All glass Glass, MEL Glass, MEL, AN
Primary-Phase Anorthite						
37.2	19.7	33.1	10	$\begin{cases} 30 \\ 30 \end{cases}$	$\begin{matrix} 1267 \\ 1263 \end{matrix}$	All glass Glass, AN, very rare MEL
Simultaneous Phases Anorthite-Melilite-Nepheline						
35.7	17.8	36.5	10	$\begin{cases} 30 \\ 30 \end{cases}$	$\begin{matrix} 1250 \\ 1246 \end{matrix}$	All glass Glass, MEL, NE, sparse AN

these solid solutions, with the possible exception of the plagioclase, makes this impossible.

The plagioclase-melilite-nepheline boundary curve was located for the purpose of obtaining data on the courses of crystallization and has been used in the present work to locate what may be called a "four-phase boundary" within the quaternary field of melilite. The technique of locating three-phase boundaries in a ternary system has been

composition (increasingly deficient in the melilite composition), the composition path of which directly hits the *melilite-plagioclase-nepheline boundary curve* in the quaternary system. Thus the location of such a point in the field of melilite, coupled with the observation of the temperature at which the plagioclase and nepheline solid solution crystal-

³¹ "The Crystallization of Haplobasaltic, Haplo-dioritic, and Related Magmas," *Amer. Jour. Sci.*, Vol. XL (4th ser., 1915), pp. 171-74.

lize, fixes two points on a crystallization path in the melilite field. As described above, the boundary curve has been located within the quaternary system, and the temperature of appearance³² of the secondary phases locates the point on the boundary curve that is "hit" by the crystallizing liquid. A line joining these two points must pass through the composition of the crystals that have separated from the liquid. The above considerations are applicable in principle to the field of nepheline, although determinations in this field have not been carried out.

Examination of Figure 6 shows three points near the pseudoeutectic in the field of melilite. These points, along with others to be subsequently discussed, are reproduced in Figure 9, which is an enlarged section of the equilibrium diagram.

If the system were ternary, the final temperature of consolidation of these three compositions would be $1,266^\circ$, and at the composition of the eutectic. Runs made on point 1 (Fig. 9) did not show nepheline until approximately $1,260^\circ\text{C}$., and plagioclase appeared at approximately $1,245^\circ\text{C}$. In point 2, plagioclase was present at approximately $1,260^\circ\text{C}$., and nepheline appeared at $1,255^\circ\text{C}$. Point 3 represents a composition in which plagioclase and nepheline solid solutions appear simultaneously and at a temperature of $1,257^\circ\text{C}$. Thus the quaternary boundary curve is encountered at a temperature of $1,257^\circ\text{C}$. for this particular initial composition. It has been shown that this boundary curve passes through the plane of 10 per cent wollastonite at $1,248^\circ\text{C}$. Assuming a linear temperature relationship, $1,257^\circ\text{C}$. is halfway between

the two reference temperatures of $1,248^\circ$ and $1,266^\circ\text{C}$.; and thus the boundary curve is encountered at approximately the plane of 5 per cent wollastonite within the subsidiary tetrahedron *AN-GEH-NE-WO*. This point will be more fully discussed in the following section, but it can be seen from examination of Figure 1 that this course of crystallization is roughly toward the SiO_2 corner of the main tetrahedron.

If the nepheline solid solutions were ternary, point 4 of Figure 9 would also



FIG. 9.—Enlarged portion of the equilibrium diagram for the system $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ - NaAlSiO_4 .

consolidate at $1,266^\circ\text{C}$. Plagioclase appears in runs on this point at $1,267^\circ\text{C}$., and melilite does not appear until the temperature has fallen to $1,248^\circ\text{C}$. Point 5; in the plagioclase field, precipitates nepheline at $1,273^\circ\text{C}$. and melilite at approximately $1,246^\circ\text{C}$., whereas in point 6 melilite appears at approximately $1,255^\circ\text{C}$. The fact that melilite does not appear in runs made on points 5 and 6 until temperatures well below that of the pseudoeutectic are reached is indicative of the rather strongly nonternary nature of the nepheline solid solutions. Even in compositions close to the pseudoeutectic, there is a considerable difference in tem-

³² If devitrified mixtures are used, this temperature is that of the simultaneous disappearance of the secondary phases.

perature between that of the pseudo-eutectic and that of appearance of the third crystalline phase, indicating that the composition of the liquid is well out of the plane of the system.

No attempt has been made to follow courses of crystallization within the fields of β - Al_2O_3 or carnegieite. In general, compositions within the field of β - Al_2O_3 will follow a path away from the Al_2O_3 corner of the tetrahedron.

THE SUBSTANCES IN SOLID SOLUTION

With the exception of quartz, all rock-forming minerals are members of solid-solution series. Pure end-members of solid-solution series are rarely, if ever, found in nature; and it has been amply demonstrated that the pure end-members are never formed in synthetic melts when there are substances present with which they may form solid solutions. The nature of the substances in solid solution in the nepheline and carnegieite of this system is unsettled, but certain data here found tend to limit the possibilities at least with respect to nepheline. The "four-phase boundary" in the melilite field has, moreover, brought to light the probable existence of a hitherto unknown "molecule" in solid solution with gehlenite.

ANORTHITE

It was earlier thought that relatively pure anorthite could form in melts containing nepheline, but it is now known that the pure end-members of the plagioclase series cannot form in melts containing both soda and lime. Although few optical data could be obtained on the feldspars because of their small size and platy habit, enough were obtained to indicate that an anorthite-rich plagioclase rather than pure anorthite is formed. Crystals formed in a mix with

but little soda (approximately 6 per cent nepheline, 62 per cent anorthite, 32 per cent gehlenite) had a maximum index that very closely matched the glass at a value of $n = 1.588$, indicating that virtually pure anorthite is here formed. At a somewhat higher soda content (16 per cent nepheline, 46 per cent anorthite, 38 per cent gehlenite), the maximum plagioclase index again matched the index of the glass, at a value of 1.586. In two mixes near the plagioclase-nepheline boundary curve maximum values of $n = 1.585$ were observed, the nepheline content here reaching 37 per cent. The value of 1.585 for the lowest observed maximum plagioclase index indicates that the anorthite content probably does not drop below 95-96 per cent in this system.

Extinction angles of 72° and 74° on two well-formed crystals were observed, as measured from the albite twinning lamellae to a . These crystals were those formed from melts with the 37 per cent nepheline content. Reference to standard tables indicates an anorthite content of approximately 98 per cent, as against 95-96 per cent on the basis of index of refraction. No discrepancy exists, however, as recent work has shown that plagioclases formed at high temperatures do not have the same composition-extinction-angle relation as do the low-temperature plagioclases, for which standard tables have been compiled.^{33, 34} Plagioclases formed at high temperatures show an apparently greater anorthite content on the basis of extinction angle, as is here evident.

³³ A. Köhler, "Die Abhängigkeit der Plagioklasoptik vom vergangenen Warmeverhalten," *Min. u. petrog. Mitt.*, Vol. LIII (1942), pp. 159-79.

³⁴ See bibliography in paper by Christoffer Oftedahl, "High Temperature Optics in Plagioclases of the Oslo Region," *Norsk. geol. Tids.*, Vol. XXIV (1944), pp. 75-78.

β -ALUMINA

The probable composition of β - Al_2O_3 has been discussed.

NEPHELINE

Several substances are known to enter into solid solution with nepheline in considerable amount. A complete series of solid solutions between KAlSiO_4 and NaAlSiO_4 exists,³⁵ but potash compounds are excluded in this study. Experimental work has shown that 35 per cent each of albite³⁶ and anorthite³⁷ are taken into solid solution. The plagioclases are sufficient to account for the excess silica, as well as the calcium that is found in natural nephelines; but A. N. Winchell³⁸ has suggested that the molecule CaAlAlO_4 may also play a part in the composition.

The high indices found by Smalley in his work on the system NaAlSiO_4 - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ³⁹ are considerably above those brought about by solid solution of anorthite in nepheline. The inversion relations of nepheline and carnegieite were also such that anorthite could not be considered as the material entirely responsible. In the present study no negative nephelines were observed; those formed from melts closest to the field of carnegieite (at approximately 60 per cent nepheline) were sensibly isotropic, those precipitated from all other melts poorer in the nepheline molecule were positive, becoming more strongly birefringent as the NaAlSiO_4 content of the liquid decreased. The nepheline indices, as in

Smalley's system, increase with increasing $\text{Ca}_2\text{Al}_2\text{SiO}_7$ content of the melt. Isotropic crystals with $n = 1.540$ were observed in the mixture at 5 per cent $\text{Ca}_2\text{Al}_2\text{SiO}_7$, 60 per cent NaAlSiO_4 , 35 per cent $\text{CaAl}_2\text{Si}_3\text{O}_8$; and values of $\omega = 1.548$, $\epsilon > 1.548$, were observed in crystals near the plagioclase-nepheline boundary curve at a value of roughly 20 per cent $\text{Ca}_2\text{Al}_2\text{SiO}_7$.

It was noted that, in mixtures from which nepheline crystallized as a primary or secondary phase and melilite as the tertiary phase, the temperature of appearance of the melilite was considerably below that of the pseudoeutectic. The interpretation was that the quaternary boundary curve between the fields of melilite, plagioclase, and nepheline solid solutions was reached in the direction of falling temperature. That is, the temperature along this boundary falls in the direction of the direction of the anorthite-nepheline-wollastonite face of the subsidiary tetrahedron, and the composition of the liquid must change in this direction upon crystallization of nepheline solid solutions. Thus plagioclase cannot be the sole substance in solid solution in the nephelines of this system. In addition, anorthite or any substance near anorthite in composition would not account for the strong nonternary tendency that is shown in the nepheline solid solutions; the plagioclase compositions lie nearly in the same plane as that of this system; anorthite, of course, lies in the plane.

It thus appears that at least part of the material entering into solid solution with nepheline lies on that side of the system that is toward the Al_2O_3 corner of the main tetrahedron. Sodium or calcium aluminates would fulfil this requirement. The CaAlAlO_4 molecule proposed by Winchell might well be a substance en-

³⁵ N. L. Bowen, "The Sodium-Potassium Nephelites," *Amer. Jour. Sci.*, Vol. XLIII (4th ser., 1917), pp. 115-32.

³⁶ P. 106 of ft. n. 7.

³⁷ P. 563 of ft. n. 4.

³⁸ *Elements of Optical Mineralogy*, Part II (3d ed.; New York: John Wiley & Sons, Inc., 1933), p. 297.

³⁹ See ft. n. 10.

tering into solid solution with nepheline in this system. It is also known that $\text{Na}_2\text{Al}_2\text{O}_4$ forms a solid-solution series with carnegieite,⁴⁰ and it is not unlikely that it can also form solid solutions with nepheline. The establishment of "four-phase boundaries" in the field of nepheline might shed more light on the exact nature of the solid solutions.

At first sight it appears peculiar that no evidence of CaAlAlO_4 and/or $\text{Na}_2\text{Al}_2\text{O}_4$ is found in naturally occurring nephelines. An excess of SiO_2 is usually present, and the above compounds would make for undersilicated nepheline. The system studied is deficient in silica, however, as compared to natural magmas, and it is likely that in magmas the silica content is always sufficient so that feldspar forms solid solutions with nepheline rather than the aluminates. It is more probable, however, that at the high temperatures of this work, probably higher than those of magmas, solid solutions form that are not found in nature.

CARNEGIEITE

This investigation has produced no new evidence as to the nature of the carnegieite solid solutions. Smalley⁴¹ has observed a marked index rise and inversion lowering in the system NaAlSiO_4 - $\text{Ca}_2\text{Al}_2\text{SiO}_7$. Inversion lowering is very unusual in silicates, as it requires a greater amount of solid solution in the high-temperature form than in the low-temperature form of an enantiotropic pair. However, as the carnegieite solid solutions undoubtedly present a problem very similar to that of the nepheline mix-crystals, the situation is perhaps not too obscure. Here anorthite is unquestionably out of consideration as the respon-

sible agent, as it is taken up by carnegieite only to the extent of 5 per cent, whereas nepheline will take 35 per cent.⁴² C. E. Tilley⁴³ found that Na_2SiO_3 entered into carnegieite solid solutions to the extent of 24 per cent but not at all into nepheline. The changes in birefringence and index rise were not consistent with those found by Smalley, however, and it is unlikely that Na_2SiO_3 plays a part in this system. Smalley found that the trend of the solid solutions was to increase in concentration with increase in the $\text{Ca}_2\text{Al}_2\text{SiO}_7$ content of the mixture and suggested that the sodium aluminate ($\text{Na}_2\text{Al}_2\text{O}_4$) was responsible; the decrease in silica brought about by the addition of gehlenite would account for the trend rather than the addition of lime, with formation of a lime-bearing solid solution. This view is in line with the discussion of the nepheline solid solutions, and, in addition, it may be that the CaAlAlO_4 molecule is also present in the mix-crystals.

GEHLENITE

The indices of the melilites that crystallize in this system are significantly lower than those of pure gehlenite. Gehlenite has indices of $\omega = 1.669$ and $\epsilon = 1.658$. The melilite formed from a mixture of composition anorthite 16 per cent, gehlenite 67 per cent, and nepheline 17 per cent had indices of $\omega = 1.665$, $\epsilon' = 1.656$; and in a composition of anorthite 38 per cent, gehlenite 32 per cent, and nepheline 30 per cent the indices were $\omega = 1.656$, $\epsilon' = 1.645$; at anorthite 5 per cent, gehlenite 37 per cent, and nepheline 58 per cent, $\omega = 1.651$, $\epsilon' = 1.641$. A progressive decrease

⁴² P. 563 of ftn. 4.

⁴⁰ Unpublished work of J. F. Schairer and N. L. Bowen.

⁴¹ See ftn. 10.

⁴³ "The Ternary System Na_2SiO_3 - $\text{Na}_2\text{Si}_2\text{O}_5$ - NaAlSiO_4 " *Min. u. petrog. Mitt.*, Vol. XLIII (1933), p. 414.

in index with increasing soda content is thus observed, a decrease that was also found by Smalley to exist in the limiting $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{--NaAlSiO}_4$ system. No decrease in birefringence was observed.

The natural melilites have complex solid-solution relations, and this complexity has elicited considerable discussion. A complete series of solid solutions exists between $\text{Ca}_2\text{Al}_2\text{SiO}_7$ and $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (akermanite); but for purposes of this discussion the magnesia-bearing varieties, as well as the iron melilites, will be neglected. In 1924, A. N. Winchell⁴⁴ took up the melilite problem from the viewpoint of volume isomorphism and largely discredited the sarcolite molecules which had been proposed earlier by W. T. Schaller⁴⁵ and partially verified by A. F. Buddington.⁴⁶ Winchell pointed out the essential R_5O_7 character of the melilites and proposed the molecules $\text{Na}_2\text{Si}_3\text{O}_7$ and $\text{Ca}_3\text{Si}_2\text{O}_7$ as theoretically capable of entering the gehlenite structure. In addition, the possibility of the presence of several sodium-aluminum silicates and a calcium-aluminum silicate was considered. Berman⁴⁷ in 1929 reviewed the problem and modified Winchell's fundamental R_5O_7 to $\text{X}_2\text{Y}_3\text{O}_7$. He also changed Winchell's $\text{Ca}_3\text{Si}_2\text{O}_7$ to CaSi_3O_7 . The melilite molecules, as seen by Berman (omitting akermanite) are shown in the accompanying tabulation.

Gehlenite.....	$\text{Ca}_2\text{Al}_2\text{SiO}_7$
Soda melilite.....	$\text{Na}_2\text{Si}_3\text{O}_7$
Submelilite.....	CaSi_3O_7

⁴⁴ "The Composition of Mellilite," *Amer. Jour. Sci.*, Vol. VIII (5th ser., 1922), pp. 375-87.

⁴⁵ "Mineralogic Notes," Ser. 3, *Bull. U.S. Geol. Surv.*, No. 610 (1916), pp. 109-28.

⁴⁶ "On Some Natural and Synthetic Melilites," *Amer. Jour. Sci.*, Vol. III (January, 1922), pp. 35-87.

⁴⁷ Harry Berman, "Composition of the Melilite Group," *Amer. Min.*, Vol. XIV, No. 11 (November, 1929), pp. 389-407.

On the basis of chemical analyses Berman stated that the "soda melilite" does not exceed 25 per cent in natural occurrences and the "submelilite" not over 10 per cent.

The location of the quaternary boundary curve between the fields of melilite, plagioclase, and nepheline solid solutions and the determination of the "four-phase boundary" discussed in the section on courses of crystallization was made principally to obtain information on the nature of the melilite mix-crystals in this system.

The essential data with respect to the "four-phase boundary" are here summarized. A liquid represented by the composition of point 3 in Figure 9, upon crystallizing melilite, hits the quaternary boundary curve at $1,257^\circ\text{C.}$, as evidenced by simultaneous crystallization of plagioclase and nepheline as secondary phases. Two points are thus located; the initial composition (point 3, Fig. 9), and that point on the boundary curve representing the composition of the liquid at the time when sufficient melilite has crystallized to attain this composition. A straight line, drawn from this point on the boundary curve through the initial composition, points to the composition of the melilite crystallizing at the time that the boundary curve is reached. The composition of the initial point is known, and that of the point on the boundary curve can be located by making the assumptions of a straight boundary curve with linear temperature drop, as earlier discussed. As the temperature is $1,257^\circ$, half of the difference between the planes of 0 and 10 per cent wollastonite can be assumed to be in the plane of 5 per cent wollastonite. Calculation of this point gives the following oxide percentages,

On the basis of this single determination, it thus appears that the 1:2 compound of lime-alumina is the substance in solid solution in gehlenite crystallizing from this system. Moreover, if any other hypothetical "molecule" enters the mix-crystals, it must do so in very small amounts.

As was postulated for the nepheline solid solution, it is again a subsilicious phase that precipitates from melts of the present investigation. No such silica-poor melilites are found in nature. Natural magmas are not comparable in composition to melts in this system, however; and, as previously discussed, the temperatures of crystallization are considerably lower in magmas. This difference of composition of the natural magmas presumably results in the formation of solid solutions of a nature other than those containing the 1:2 molecule, and the understanding of the complexity of the melilites is by no means completely resolved by this investigation.⁵⁰

identification of secondary phases (1, above) would be more difficult.

3. The assumption of a straight boundary curve with linear temperature drop is not strictly true.

4. There are experimental errors of temperature measurement and composition synthesis.

⁵⁰ Although the results of this investigation as interpreted above indicate solid solution of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ in gehlenite, certain difficulties are encountered in this supposition. No solid solutions of this nature were encountered in the investigation of the system $\text{CaO--Al}_2\text{O}_3\text{--SiO}_2$ (ftn. 26). The proposed substitution of Al for Ca in the solid solutions is rather doubtful, owing to the small size of the Al atom. It is therefore important to note that another interpretation is possible: if a maximum temperature is present on the melilite-nepheline-plagioclase boundary curve, the melilites crystallizing from this system may be enriched in Si and Na. Thus, if a temperature of $1,257^\circ$ exists on the low-silica side of the plane of the system, the "molecule" in solid solution in gehlenite could be the $\text{Na}_2\text{Si}_3\text{O}_7$ proposed by Berman, which, it must be admitted, is more likely from a structural point of view. It is hoped that this point can be cleared up in a future investigation.

PETROLOGIC SIGNIFICANCE

Complete knowledge of the equilibrium relations within the soda-lime-alumina-silica system is of great importance in the understanding of the problems of igneous petrology, and the present paper is a contribution toward that end. These four oxides constitute, by weight, 90 per cent of the average of 546 granites, 85 per cent of the average of 43 nepheline syenites, and 77 per cent of the average of 161 basalts.⁵¹ The minerals—quartz, plagioclase feldspars, nepheline, wollastonite, gehlenite, corundum, sillimanite, mullite, grossularite, larnite, and jadeite—are formed of these four oxides, although the last five are formed only under "metamorphic conditions." Knowledge of the four oxide systems is also of prime importance in certain technological fields.

The equilibrium relations as determined in this study contribute to the knowledge of the relations within the main system. All seven faces of the subsidiary double tetrahedron have now been investigated.^{52, 53} It has been mentioned that the melts within the plane here studied do not correspond in composition to any natural magmas. The closest approach is to be found in magmas that formed certain basic alkaline rocks, such as the tephrites, melilite-nephelinites, urtites and ijolites, turjaïtes, and melilite basalts. All these rocks contain greater or lesser amounts of a pyroxene and numerous accessory

⁵¹ R. A. Daly, *Igneous Rocks and the Depths of the Earth* (New York: McGraw-Hill Book Co., Inc., 1933, pp. 9-28).

⁵² See bibliography in paper by N. L. Bowen, "Phase Equilibria Bearing on the Origin and Differentiation of Alkaline Rocks," *Amer. Jour. Sci.*, Vol. CCXLIII A (Daly Vol.) (1945), p. 83.

⁵³ The anorthite-gehlenite-wollastonite face is based on unpublished work of V. C. Juan.

minerals. The melilite of this system is also less complex than the natural mineral, because of the absence of magnesia and iron.

The strong tendency of gehlenite, nepheline, and anorthite to form solid solutions is again demonstrated in the present study; and, because of the non-ternary nature of the solid solutions, the system must be considered in terms of the four constituent oxides. Crystallization of the nepheline and melilite solid solutions results in a liquid enriched in SiO_2 and Na_2O ; and, once the quaternary boundary curve between the fields of melilite, plagioclase, and nepheline is reached, fractional crystallization could carry the residual liquid toward the plane of anorthite-nepheline-wollastonite, which is common to the subsidiary double tetrahedron. The fact that the field of melilite plunges through this boundary face, as discussed by Bowen,⁵⁴ results in a quaternary reaction point within the adjoining tetrahedron, anorthite-wollastonite-nepheline-albite, and permits fractionation to continue so that residual liquids within this portion of the

main tetrahedron can result. Bowen⁵⁵ points out that fractionation can continue until the liquid reaches a composition within that portion of the quaternary system outlined by the compounds nepheline-albite-devitrite ($\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_6$)-sodium disilicate, the crystalline assemblages running the gamut from simplified melilite-nephelinites through simplified tephrites and phonolites to alkali rhyolites, with a soda-rich liquor remaining.

The encroachment of a field of alumina upon the anorthite-nepheline join is suggestive in connection with the occurrence of corundum in certain anorthosites and nepheline-bearing syenites.

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⁵⁴ See reference cited in ftn. 52.

⁵⁵ See reference cited in ftn. 52.

